Atomic stiffness parameter: A guide for patterning nanostructures

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1. Atomic stiffness parameter: A guide for patterning nanostructures

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Abstract: The atomic stiffness parameter (ASP) in dense phases: $S = 9vB\varepsilon^{-1}$ where v stands for atomic volume, B for bulk modulus and ε for atomic cohesive energy expresses the competition between metallic attraction and core-core repulsion. ASP is driven by the repulsive interaction between electronic more or less filled internal shells since attractive metallic bonding is common for all metals. The square root of ASP was early introduced as anharmonicity parameter η by Rose *et al*. ASP controls the occurrence of local defects in crystalline structures. Since crystalline defects are essential for cluster structures, surface rearrangements and grain boundary structures, i.e. nanostructures, ASP also controls bulk malleability and ductility. The ASP set of composite materials controls their tendency to form quasicrystals and amorphous materials. Nanometric friction between materials also depends on respective ASP values. ASP values define several classes of metals, according to their ability to bear non-homogeneity. So called "extra stiff" metals have completely filled internal electronic shells, noble metals are "very stiff" while numerous metals are more or less smooth. This stiffness classification is linked with structural properties of nanostructures.

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1. Introduction

The rather recent observations of atomic clusters prepared within a high vacuum chamber or in an inert gas [1-3], or elaborated from soft chemistry [4,5] as well as the observation of metallic surfaces analyzed at a very atomic level [6,7] have revealed quite numerous new structural features for assembled pure elements in clusters, nanowires and organized surfaces. Among these features, cluster magic numbers, nanowire magic numbers and the occurrence of surface rearrangements even for pure materials are well known. For the structure of clusters, nanowires, surfaces and generally nanostructures, the part of local defects in front of crystalline structure is important. It must be added that, for composite materials, the recent observation of new stable or metastable states such as quasicrystals [8,9] or amorphous packing [10,11] obtained after a more or less rapid quenching gives a way for comparing the very atomic properties of elements. These numerous observations suggest several possible classifications of metallic elements from their basic properties in dense phases. Since metallic attraction is common for metals, the driving factor of local structure comes from core-core repulsive interaction. So the goal of this paper is to introduce a parameter linked with core-core interaction which enables us to deduce a simple classification of metallic elements according to experimental results. Finally the existence of such a valid classification enables us to extrapolate present results and to suggest complementary experiments.

The comparison of metallic elements requires a simple local approach even if metallic interaction involves a collective approach of Fermi electronic sea [12]. Elaborate approaches such as various density functional theories [13] or embedded atom models with non local interactions [14] are now currently used for calculating the structures and properties of bulk metals or small clusters for each element. The comparative approach to be developed here must be simpler than these detailed approaches and must be focused on a very local picture. Such a local approach corresponds to an effective pair potential approach well known to describe simple effects observed on clusters [15] and on surface rearrangements [16-18]. The simplest ingredients for such an approach are atomic volume v, cohesive energy per atom ε and bulk modulus B as could be considered for pair potential interactions of rare gas in dense phases [19].

In crystalline dense phases two elements A and A' of respective atomic volumes v and v' and similar crystallographic structure have a lattice mismatch which is proportional to: $v^{-1/3}$-$v'^{-1/3}$. This lattice mismatch is responsible for Moiré observations of non alloyed interfaces by electronic

microscopy [16, 20] and for the formation of Stranski-Krastanov islands when depositing A' over A [16, 21]. This effective lattice parameter $v^{1/3}$ is purely geometrical.

Atomic volume v and cohesive energy per atom ε define a density of surface energy of an element which is proportional to $\varepsilon v^{-2/3}$. The differences between respective densities of surface energy of immiscible elements define surface tensions [21], which are energy per surface, i.e. force per length.

A third local parameter is associated with the stiffness of the total interaction $u(v)$ between atomic units, i.e. results from the competition between attractive and repulsive contributions. This is the bulk modulus which is easily defined for an isotropic material as $B = v\frac{d^2u}{dv^2}$ [22]. So a pure numerical local parameter, the atomic stiffness parameter (ASP) is deduced from the combination of v, ε and B:

$$S = 9\frac{vB}{\varepsilon}\cdot \qquad (1)$$

The choice of the constant comes from calculations done for pair potential interactions. These pair potential interactions enabled us to extend the work done on rare gas since Lennard-Jones [19] to other dense phases. This has been done with two-exponents radial pair interactions [15-18]. Models derived from these three parameters v, ε and B well describe interface properties, for instance Monte-Carlo simulations using such models evidenced the so numerous Pb/Cu (100) superstructures [16-18] where large lattice mismatch interplays with strong stiffness difference. ASP is just the square of the so-called anharmonicity parameter η introduced in the zero temperature equation of states of metals [23] and now considered in embedded atom models [24]. Table 1 of reference 23 gives the anharmonicity parameter for most metals. The name anharmonicity parameter given in ref. 23 emphasizes on the dissymmetry between metallic attraction and core-core repulsion, while the name ASP focuses on resulting properties which are more obvious in comparing these elements together.

Since each parameter v, ε and B weakly depends on temperature, ASP also depends on temperature. Yet for a given dense phase this variation is rather restricted. So the deduced accuracy of ASP defines classes of elements more than individual properties.

Quite obviously several further steps could be introduced in this minimalist description of metals. Still at a local atomic level, atomic skewness, i.e. anisotropy at a very atomic level must be introduced as it has

been already pointed out about clusters [25]. This anisotropy effect already occurs when discriminating hexagonal close packed (hcp) structures from face centred cubic (fcc) ones which lead to the same crystalline density. Numerous anisotropic growths must have their origin in such terms.

Non local effects such as the properties linked with band structure must also appear as classifying properties. Bandwidth and a parameter linked with band shape can be easily defined. However since attractive metallic interaction is common for all metals, the main difference between metals just comes from their repulsive interaction, i.e. the core-core interaction. So the analysis of ASP values to be done here is a good basic first tool for classifying metallic elements.

In this paper section two is devoted to the classification of metallic elements according to their atomic stiffness parameter in agreement with physical properties for clusters, nanowires and surfaces. Section three focuses on the new consequences introduced by this classification both on experimental and theoretical points. The derivation of ASP for pair potentials is recalled in appendix.

2. ASP values and atomic stiffness classification

ASP classification is sensitive to core-core interactions. An atom with filled internal electronic shells is stiffer than one with unfilled electronic shells and so on. The filling of external electronic shells defines successive columns in Mendeleiev's periodic table. Then an increase of the number of internal shells for elements within the same column leads to a subsidiary increase of stiffness. So ASP increases with line number in periodic table. Finally ASP classification is close to Mendeleiev's classification but mixes lines and columns in a slightly slanted way as shown in Table 1, ref. 23. It must be kept in mind that this atomic stiffness is not directly related to macroscopic hardness.

The main interest of this classification is the evidence for common properties for equal or nearly equal ASP values, i.e. the evidence for material classes. The physical meaning of a variation of ASP value corresponds to a variation in the difficulty to produce crystalline defects. For composite materials, it gives an idea about the part where defects can be localized. Here just a few ASP classes are distinguished by the sake of simplicity.

Table 1. Atomic stiffness parameter for "very stiff" metals.

Element	Hg	Cd	Zn
S	49.75	48.7	37.8

2.1. Very stiff metals

The class of metals with very large ASP values is the class of elements with ground state filled external shells, with the final structure (ns^2, (n-1) d^{10}). For these "very stiff" metals, atomic stiffness has just an atomic meaning, it means that these metals have nearly no defect in their dense phase. In the words of ref. 23, these very stiff metals have a very strong anharmonicity.

This local stiffness is linked with a low cohesive energy and an easy melting. The increase of ASP with increasing line number is well observed in this table. The specific features of this class of metals are the formation of crystalline clusters, crystalline nanowires and crystalline surfaces with rare defects as well as the elastic properties of alloys.

2.1.1 Very stiff metal clusters

The cluster properties of mercury prepared in inert gas have been studied both experimentally [26] and numerically [27] because of the interest for a transition from Van der Waals clusters to metal clusters [28], i.e. from molecular cluster with discrete energy levels to metallic clusters with an energy band. It appeared that the transition from an icosahedron of 13 atoms to a block of several crystalline parts happens very early for these mercury clusters. This is in good agreement with the present notion of atomic stiffness which means a difficulty to create defects and non homogeneities which occur in icosahedral arrangements [18]. Cadmium clusters Cd_n show an icosahedron for n=13 and uncompleted double icosahedron for n<18, then for larger sizes, cadmium clusters are close packed multicages which are assumed to be metallic when n>20 [29]. This is the characteristic behaviour of a very stiff metal with an early transition towards crystalline structure. The behaviour of Zn_n clusters is rather similar to that of Cd_n clusters [29, 30].

2.1.2. Nanowires of "very stiff" metals

Nanowires can be considered as anisotropic clusters and so are similar to clusters from the point of view of their organization. The existence of well crystallized nanowires for these "very stiff" metals is another proof of the difficulty to create defects in these metals. Cadmium nanowires have been recently prepared by means of different techniques, such as sputtering [31]. According to substrate temperature, disks can also be produced, i.e. another cluster geometry. The study of nanowires in very stiff metals is just beginning and the few available results must be compared with results for other classes.

2.1.3. Surface structures of “very stiff” metals

Surface properties of these polluting elements are not well known. Since very stiff metals do not support easily defects, surface reconstructions in crystalline parts are expected to occur for these materials. One main result of this analysis is to emphasize the interest of such experimental and theoretical work.

2.1.4. Elastic properties of very stiff metals in alloys

Brass, i.e. copper-zinc alloy has been well known since prehistory for its hardness. Now it is well known that this hardness is increased when brass is rich in zinc. Recently very stiff amorphous metals have been produced, and they are zinc rich [11]. So even in this class of rather less-studied metals, the concept of atomic stiffness is quite obvious, even if more information is required.

2.2. Noble metals

The second class of metals according to their stiffness property contains less filled external shells (ns^1, $(n\text{-}1)d^{10}$) in the ground state and some near electronic variants, i.e. noble metals in a large sense. In the words of ref. 23 these metals have a strong anharmonicity. These elements are known to be noble from their chemical properties, i.e. their weak chemical reactivity. As a consequence highly purified samples are available. An interesting property of these materials comes from the variation of their excitation spectrum and of their optical plasmon frequency with cluster size. This has several applications. Another of their practical properties due to their electronic richness is their catalytic power which is responsible for numerous works on their cluster and surface properties. Finally among the large number of electrons of these elements, some of them have relativistic properties which induce noticeable spin-orbit coupling. So, small clusters of these metals often show interesting magnetic properties.

These ASP values are sensibly lower than the ones of very stiff metals. These values are shown to increase when increasing element line number as expected. As already noticed, there is no direct connection between atomic

Table 2. Atomic stiffness parameter for noble metals.

Element	Au	Os	Ir	Pt	Re	Pd	Rh
S	43	41.7	40.7	40.2	38.2	38.3	36.4

stiffness and macroscopic hardness even if osmium has a very high bulk modulus value.

2.2.1. Noble metal clusters

Gold clusters have been studied experimentally quite extensively since a long time as prepared in high vacuum from atomic beam [32]. Gold clusters have been also prepared by chemical means, i.e. in contact with liquids [33] or within an inert gas environment by means of jet and nozzle techniques [34]. Gold clusters have also been prepared within alumina nanopores [35], i.e. under high constraints. Several numerical methods have also been used to derive the stable and metastable states of gold clusters. From theoretical work, gold clusters are expected to be planar in their ground state up to n=12 [3, 36, 37]. At n=13 an icosahedral structure is expected and after that, assembled parts of fcc crystals are expected to give the ground state, while icosahedral structures are observed up to n<500 probably because of kinetic effects. Larger clusters which have been observed since the early sixties [32] have shown a famous multi-twinned fcc structure with icosahedral or decahedral global shapes. As already said about mercury clusters, such observations of an early transition towards crystalline structure are in good agreement with the ASP notion of a stiff or very stiff metal in the atomic meaning. The transition towards a crystalline structure occurs here for very small cluster sizes.

Platinum clusters and other metal clusters of this class have been extensively studied because of their catalytic activity [38]. This has been done first in wet chemical conditions, with soft chemistry [39]. Platinum clusters have also been produced by the nozzle technique within an inert gas [40]. They have been also prepared within zeolite cages [41]. Platinum is expected to lead to an icosahedral structure at a very low size such as Pt_{13}. From recent ab initio studies using density functional theory, very small platinum clusters are planar up to n=9, then layered pyramidal in the range n=10-20, then decahedral in the range 21-24, simple cubic up to n=38 and then fcc [42]. This expresses a strong tendency towards crystalline structure as observed for gold. The comparison with gold and very stiff metals reveals an effective lower atomic stiffness for platinum. It must be added that due to the large number of platinum core electrons, relativistic effects and thus spin orbit coupling effects are strong. So, platinum clusters are expected to show interesting magnetic properties, at least when platinum is coupled to magnetic elements.

For other noble elements, the cluster structure has been less studied, even if some recent results evidenced planar structures and magnetic properties of

iridium and palladium clusters composed of a few atoms [43], well in agreement with the properties of this class of metals.

2.2.2. Noble metal nanowires

Gold nanowires have been produced from STM studies by extracting wires made of one or several strands between two tips [44]. These nanowires exhibit helical multi shell structures made of several strands surrounding a central strand with successive shells according to a magic order: 1-7, 4-11, 6-13, 1-7-14 where in the first case one strand is surrounded by seven strands. These "weird" structures exhibit a higher density at the surface than in the inside, as it appears for gold surface reconstruction. These nanowires show ballistic conductance according to Landauer's formula [45]. The very simple 1D gold chain exhibits a strong dilation of its lattice parameter in front of the distance between neighbouring gold atoms in dense phases [44]. These new fascinating complex structures received a lot of theoretical interest [46]. Gold nanowires have also been produced by chemical means in nanoporous ion track membranes [47]. This topic is now leading to a new field comparable to that devoted to carbon nanotubes.

A similar shell structure has been observed for platinum nanowires obtained from electron beam thinning method followed by stretching of the platinum wire [48]. This time six platinum strands are formed around an unoccupied wire axis, a 0-6 structure, and the following optimal structure is a 0-6-13 one where a crown of thirteen strands surrounds the central part. Thus there is also a higher density at the surface than inside. A fully-relativistic pseudopotential density functional theory proved that short platinum nanowires are magnetic [49].

Rhenium nanowires [50] have been recently studied theoretically and they exhibit similar structural properties as well as magnetic properties as platinum nanowires. Thick rhenium nanowires have also been produced and mechanically tested [51].

Rather thick palladium nanowires have been produced by pulsed electrodeposition using anodized aluminium oxide nanotemplate [52] or by electroless deposition on a porous stainless steel template [53]. Theoretically, a single-strand palladium nanowire is expected to be magnetic [54].

So there are numerous results which show that noble metals can be used to make ultrathin nanowires. Ultrathin nanowires often show a special, "weird" shell structure, i.e. a strong surface reconstruction. And unusual magnetic properties occur for these nanowires made of atomic elements with so many electrons.

2.2.3. Noble metal surface properties

Gold is known for a famous herringbone surface reconstruction for (111) plane [55] with surface denser than bulk. Platinum is also known for a rather similar surface reconstruction under platinum gas pressure [56]. A theoretical understanding of gold reconstruction has been obtained by mixing ab initio calculations and Frenkel- Kontorova's model considerations on elastic energy [57]. Less is known from the surface properties of other noble metals. Recent interaction models used for describing gold herringbone reconstruction emphasized the repulsive character of filled electron shells [58] in good agreement with the present picture.

Gold also exhibits specific nanofriction properties as observed in surface tunnelling microscopy [59]. Gold atoms are easily taken off the substrate and soon appear as crystal parts on the cantilever [59], with a rather high stiffness. This is also the basis for production of ultrathin gold nanowires [44] and platinum nanowires [48].

2.2.4. Noble metal elastic properties in alloys

These noble metal stiff materials appear rarely in the composition of quasicrystalline compounds or in amorphous materials and when it happens they have just a very low concentration among other constituents. This observation is in good agreement with the noticed large atomic stiffness of these metals as shown from their ASP values.

2.3 Stiff metals

This class includes several heavy metals of right columns in the periodic table. These classified metals show a high level of anharmonicity in the sense of ref. 23.

As expected from previous considerations this classification corresponds to a slightly slanted cut of Mendeleiev's table, i.e. different columns and lines are mixed.

Table 3. Atomic stiffness parameter for stiff metals.

Element	Pb	Mo	Ru	Tc	Ag	W
S	36	35	35	34.6	34	31.2

2.3.1. Clusters of stiff metals

In ab initio calculations [60], lead clusters Pb_n follow an oblong growth pattern from n=14. Layered stacking structures are observed in the size

range of n=13-18. These properties are quite comparable to those observed for “noble metals”, as expected from ASP value. Experimental evidence is restricted to higher cluster sizes and depends on the used inert gas mixture [61]. To our knowledge there is no experimental or theoretical data on molybdenum clusters. Ruthenium clusters Ru_n were produced and seen to be magnetic in the range (n=12-32) [62]. Theoretical calculations confirmed this observation in the range (12-43) and showed that there is a contraction from 3 to 8% according to the cluster size and there is a transition from icosahedral structure to cub-octahedral structure for $n<43$ [63]. To our knowledge there is no experimental or theoretical study of technetium clusters.

Because of their practical interest in photography, silver clusters and their optical properties have been studied since a long time [64]. From theoretical ab initio studies, their structure for $12<n<22$ is dominated by icosahedral constructions [65]. Silver clusters also exhibit magnetic properties [66].

Optical studies of very small tungsten clusters were performed early with attention to photoemission, dissociation and thermionic emission [67].

2.3.2. Nanowires of stiff metals

Romanov produced lead nanowires inside the natural zeolite mordenite and observed their conductivity properties [68]. Several authors studied theoretically the structural and electronic properties of these lead nanowires [69]. They found that the maximum binding is obtained for the caged and helical nanowires. So this structure is close to that observed for gold and platinum nanowires [44, 48] which are made of several strands.

There is no literature about ultrathin molybdenum nanowires. Of course there are many productions of metallic nanowires for connective purposes as well as for catalysis. There is also an interest in making photonic devices made of arrays of nanowires [70]. Here we want to focus on nanowires of atomic width which are produced from mechanical thinning and exhibit Landauer’s ballistic conductivity [45]. Among them, silver nanowires [71] are comparable to gold nanowires [44]. These silver nanowires are nanotubes made of crystalline parts [71]. And similar silver nanowires were produced from soft chemistry [72].

Numerous numerical simulations on these “crystalline” nanowires were performed and proved that, at least for a single strand, Ag, Mo, Tc, W and Re nanowires are antiferromagnetically ordered while Ru, Rh and Ir single stranded nanowires show ferromagnetic order [73]. This magnetic

classification just reproduces the proposed ASP classification as well as the anharmonicity one [23].

2.3.3. Stiff metal surface properties

As already said, there is no surface reconstruction of stiff metals for simple surface directions. However for more complex "vicinal" structures, some theoretical studies of surface reconstructions were done for lead [74], according to modified embedded atom models (MEAM) [75]. Since lead is a familiar metal with a rather low melting temperature, numerous experimental surface studies of lead coatings on well defined surfaces have been performed. Lead on silicon and germanium (001) is known experimentally to lead to numerous well defined phases c(4x8)-α and c(4x8)-1 [76].(2x2) (2x1) c(4x4) and c(4x8) [77]. There are also many well defined phases for lead deposited on silicium (111) [78]. Quite numerous studies of lead deposited over copper with different surface orientations, different deposition temperatures and different layer concentrations show a large number of new phases [79-83] which evidence the effective stiffness of lead atoms [17-18] as compared to copper atoms which look rather smooth by comparison.

Quite similarly numerous studies have been devoted to the case of silver deposited over the (111) surface of silicon [84-86], at least for electric connection. Numerous new phases were observed. These phases are quite different from that observed for gold deposition and are quite similar to the ones observed for lead deposition.

The (100) surfaces of molybdenum and tungsten are known to exhibit a low temperature reconstruction [87]. Numerous theoretical works on lattice dynamics were used to explain these structural transitions which well reveal the atomic stiffness of molybdenum and tungsten.

2.3.4. Stiff metal elastic properties in alloys

Several lead alloys were considered because of lead superconductivity. Alloys mixing mercury and lead have a low melting point and have rather high bulk modulus which is consistent with respective ASP values.

Molybdenum is used for strengthening alloys such as steel alloys.

Ruthenium appears in quasicrystals such as Al-Ni-Ru [88] or Al-Cu-Ru [89] where its size and stiffness are complementary to that of aluminium and nickel or copper. Rather similarly, quasicrystalline Al-Pd-Tc structures have been obtained by rapid quenching because of the complementary nature of technetium. Numerous quasicrystalline structures were found with silver and

among them Ag-In-Cu, Ag-In-Cu-Mg, Ag-In-Yb, Ag-In-Yb-Mg [90] and ZrAlNiCuAg [91].

Numerous bimetallic cluster structures have been observed. If core-shell separation is dominated by the difference in melting temperature, stiffness differences also contribute to segregation [92, 93].

These stiff metals share numerous properties, but many of them are still unknown.

2.4. Moderately stiff metals

This class includes metals of middle columns in the periodic table. These metals are classified according their ASP value. These metals have a moderate level of anharmonicity in the sense of ref. 23.

Table 4. Atomic stiffness parameter for moderately stiff metals.

Element	Ti	Tl	Co	Ni	Fe	Cu	Ta	In
S	31.2	30.5	27.2	26.6	26	26	25	23.9

2.4.1. Moderately stiff metal clusters

A few studies have been devoted to titanium clusters [94].

Cobalt clusters have been intensively studied because of their strong magnetic properties which were observed [95]. Modelling strongly depends on involved models. It seems that models which take into account magnetism favour distorted crystalline structures even for very small clusters [96] while non magnetic models lead to usual icosahedral structures. Nickel clusters also exhibit magnetism with a larger magnetization than bulk magnetization [97].

Iron clusters also exhibit superparamagnetism with a larger magnetization than bulk magnetization [98] and structural problems.

For copper clusters, in situ diffraction gives evidence of icosahedral order up to a size of 500 atoms and then dihedral order appears, before a further transition towards fcc structure at a size of about 700 atoms [99]. This is well in agreement with the rather soft character of copper atoms.

Finally for magnetic atoms there is a serious magnetic contribution to cluster symmetry.

2.4.2. Moderately stiff metal nanowires

Titanium nanowires with magic numbers were observed [100].

Production of cobalt, nickel and iron nanowires is actively pursued because of magnetic applications. For the time being, only rather thick wires are produced.

Single stranded copper nanowires [101] have been produced recently in a way similar to that used for gold [42]. So nanowires of moderately stiff metals seem to be interesting for realistic projects since they can be produced and have a regular structure as clusters show.

2.4.3. Moderately stiff metal surfaces

Titanium is present under different phases. There is no surface reconstruction for low index cuts of titanium.

There is no surface reconstruction for cobalt, nickel and iron. These observations are in agreement with this moderate atomic stiffness.

2.4.4. Moderately stiff metal elastic properties in alloys

These metals are present in numerous quasicrystals without being major parts in them, well in agreement with their moderate stiffness. The existence of layered alloys mixing metals of different stiffness such as FePt or CoPt is well in agreement with the optimal 2D triangular packing and the consequent 3D laminated packing [102]. And such layered materials where magnetic layers alternate with non magnetic ones with large spin-orbit coupling can result in artificially very hard magnets.

2.5. Soft metals

This class includes metals of middle columns in the periodic table. These classified metals show a low level of anharmonicity in the sense of ref. 23. The difference in ASP values with previous classes is quite large.

Table 5. Atomic stiffness parameter for moderately stiff metals.

Element	U	Al	Zr	Yr	Mn	Be	Ce
S	20.8	20.6	17.4	15.5	14	13	10.7

2.5.1. Soft metal clusters

Aluminium clusters evidence magic numbers [103] with a shell structure and a rather low symmetry for already 55 atoms [104]. Their melting properties [105] show several steps: premelting and melting, in agreement

with the shell assumption. These properties confirm aluminium smoothness as shown from ASP.

Manganese clusters exhibit size dependent magnetic properties [106]. For 13-atoms and 19-atoms clusters magnetization is quite low in front of that found for other sizes. This is an indication for an icosahedral structure for these two sizes while more complex structures are observed for other sizes. Numerous theoretical calculations have been done on these magnetic properties after this observation. The structural point well exhibits this atomic smoothness. There is also evidence for icosahedral cerium cluster for 13 atoms. And cerium has a very low ASP value. It seems that icosahedral order soon disappears in these soft materials at the benefit of a low order. Crystalline structures are expected to appear for larger cluster size. Thus the atomic smoothness destabilizes crystalline structures for medium sized clusters.

2.5.2. Soft metal nanowires

Aluminium nanowires have been obtained with evidence for ballistic conductance and for magic numbers, i.e. a shell by shell construction [107]. There is no similar study for other soft metals.

2.5.3. Soft metal surfaces

Beryllium surfaces (0001) and $(10\bar{1}\bar{0})$ show a very large thermal expansion as compared to bulk expansion [108]. This seems to be due to beryllium smoothness.

Calculations on surface structures of cerium in phase α and γ [109] also show the effects of cerium smoothness.

2.5.4. Soft metal elastic properties in alloys

Aluminium, manganese and other members of this class of atomically smooth metals are basic ingredients of quasicrystals. Quite obviously their smoothness is convenient to fit with the local non-homogeneity which is required for such quasicrystalline arrangements.

Similarly enough, zirconium is a basic ingredient in metglasses, i.e. glassy metals. This is also well in agreement with its atomic smoothness.

3. Conclusions

First, quite numerous observations and optimal calculations confirm the simple classification suggested by measured ASP values. This is a good index for its validity.

Secondly, quite numerous observations and therefore calculations are still missing. This is a challenge for future. And a simple reading reveals many interesting points to be analyzed.

Nanowires of very stiff metals such as mercury, cadmium and zinc are expected to be well crystallized with "weird" structures. These nanowires would be convenient for ballistic conductivity.

Surface reconstructions of very stiff metals are also expected to occur under convenient conditions. This could have practical applications for nano-magnetic devices supported on such oriented surfaces.

And very stiff materials could be used for hardening other materials.

Nanofriction properties of very stiff metals are of interest for designing nanowires.

Surface reconstructions of osmium, iridium could happen and provide template structures for nano magnetic devices.

About soft metals, information about rather large clusters 50-500 atoms large is lacking. And this analysis shows that such clusters could exhibit some intermediate symmetry as well as the nanowires of these soft metals.

Finally there is a general agreement between the ASP classification and observed properties. A special feature results from magnetic interactions which induce anisotropy at least in intermediate structures such as clusters and nanowires.

Appendix: ASP for pair potentials

A two exponent (*n,m*) pair potential has the form:

$V_{n,m} = \varepsilon \frac{q^n - nq}{n-1}$ with $q = \left(\frac{\sigma}{r}\right)^m$ where σ is the interatomic distance of the isolated pair at equilibrium and ε is the pair interaction energy. All atoms in the lattice share the same energy $E_{n,m}$ which is a function of the lattice parameter *a*, while interatomic distances are defined by $r_j a$ where numbers r_j are defined by the lattice geometry. So this atomic energy is $E_{n,m} = \frac{1}{2}\frac{\varepsilon}{n-1}\left(x^n S_{nm} - nxS_m\right)$ with $x = \left(\frac{\sigma}{a}\right)^m$ and lattice sums defined by $S_m = \sum_j \left(\frac{1}{r_j}\right)^m$. Optimizing this atomic energy as a function of *x* gives the optimal values of the lattice parameter and of the atomic energy of the lattice by $x_{\min} = (S_m / S_{nm})^{1/(n-1)}$ and $E_{\min} = -(1/2)\varepsilon S_m \left(S_m / S_{nm}\right)^{1/(n-1)}$. Calculating the second order derivative of the atomic cohesive energy as a function of lattice

parameter *a* for fcc lattice gives the final relation between bulk modulus atomic volume and cohesive energy per atom:

$$B = \frac{nm^2}{9v}\left|E_{n,m}\right|$$

These calculations can be applied to real clusters when neglecting boundary, i.e. surface, effects. However lattice sums strongly depend on the cluster size, specially for low exponents, so lattice parameter, cohesive energy and bulk modulus depend on cluster size.

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